Theissen

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[54]	2-NITRO-5-(CYANO-TRIFLUOROMETHYL- PHENOXY)BENZOIC ACIDS AND ESTERS		[58] Field of Search				
[75] [73]	Inventor: Robert J. Theissen, Assignee: Mobil Oil Corporati N.Y.	Westfield, N.J.	[56] 3,420,892	References Cited UNITED STATES PATENTS 1/1969 Martin et al			
[22] [21]	Filed: Jan. 29, 1975 Appl. No.: 545,232 Related U.S. Application	Data	Primary Examiner—Lewis Gotts Assistant Examiner—Dolph H. Torrence Attorney, Agent, or Firm—Charles A. Huggett; Hastings S. Trigg				
[63]	Continuation-in-part of Ser. No. 3 1973, Pat. No. 3,941,830, which is Ser. No. 114,712, Feb. 11, 1971, I which is a continuation-in-part of April 25, 1969, Pat. No. 3,652,645	s a continuation of Pat. No. 3,784,635, Ser. No. 819,412,	esters salts,	ABSTRACT substituted-phenoxy) benzoic acids and amides, and acyl halides thereof comprise a npounds that are highly effective herbicides.			
[52] [51]	U.S. Cl			2 Claims, No Drawings			

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2-NITRO-5-(CYANO-TRIFLUOROMETHYL-PHENOXY)BENZOIC ACIDS AND ESTERS

CROSS-REFERENCE TO RELATED **APPLICATIONS**

This application is a continuation-in-part of copending application Ser. No. 398,610, filed Sept. 19, 1973 now U.S. Pat. No. 3,941,830, which is a continuation of 10 copending application Ser. No. 114,712, filed Feb. 11, 1971, now U.S. Pat. No. 3,784,635, which is a continuation-in-part of application Ser. No. 819,412, filed Apr. 25, 1969, now U.S. Pat. No. 3,652,645.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is concerned with certain phenoxybenzoic acid compounds and their use as herbicides.

2. Description of the Prior Art

It has been proposed to use as herbicides 2-methoxybenzoic acids (U.S. Pat. No. 3,013,054) and 4-phenoxybenzoic acids (France, Pat. No. 1,502,538). It is the discovery of this invention, however, that benzoic acids having a phenoxy substituent in the 5-position are very effective herbicides.

SUMMARY OF THE INVENTION

This invention provides herbicidal compounds having the formula:

$$O_2N$$
 O_2N
 O_2N

wherein X is a member selected from the group consist- 40 ing of hydrogen, halogen (e.g., iodine, fluorine, chlorine and bromine), nitro, trifluoromethyl, cyano, COOH,

(e.g. alkyl of 1 to 4 carbon atoms), hydroxy, alkoxy of 1 to 4 carbon atoms, alkyl of 1 to 4 carbon atoms,

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methyl

thyl)phenoxy]benzoate;

SH, SR₁, SOR₁, SO₂R₁, SO₂NH₂ and combinations thereof, R₁ and R₂ are selected from the group consisting of alkyl of 1 to 4 carbon atoms, R is selected from 60 the group consisting of hydroxy, alkoxy of 1 to 5 carbon atoms, aryloxy, chloro, amido, alkylamido of 1 to 4 carbon atoms, dialkylamido of 2 to 6 carbon atoms, SH, SR₁, and OM in which M is an alkali metal (eg., lithium, sodium and potassium), alkylammonium of 1 65 to 4 carbon atoms or alkanolammonium of 1 to 4 carbon atoms, n is an integer of 1 to 5, and in which compound at least one X is other than hydrogen; their use

as herbicides; and a herbicidal composition comprising at least one of said compounds and a carrier therefor.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The compounds of this invention are readily prepared by the Ullmann ether synthesis reaction between the alkali metal, (eg., Na, K) salt of a suitable substituted phenol and a 5-halo (eg., F, Cl, Br)-2-nitrobenzoic acid or an ester, amide, or salt thereof. The 5-halo-2-nitro-benzoic acid or ester is readily prepared by nitrating a m-halotoluene, followed by oxidation of the methyl group by well-known procedures. Also, the m-halobenzoic acid or ester may be directly nitrated by well-known procedures.

Non-limiting examples of the compounds of this invention are:

2-nitro-5-(2',4',6'-tribromophenoxy)benzopropyl ate;

2-nitro-5-(2',4',5'-trifluorophenoxy)benzophenyl

2-nitro-5-(2',4',6'-triiodophenoxy)benzoic acid; 2-nitro-5-(2',4',6'-trichlorophenoxy)benzoyl chlor-

2-nitro-5-(2',4',6'-trichlorophenoxy)benzamide;

N-ethyl 2-nitro-5-(2',4',6'-trichlorophenoxy)benzamide:

N-isopropyl 2-nitro-5-2',4',6'-trichlorophenoxy)benzamide;

N,N-dimethyl 2-nitro-5-(2',4',6'-trichlorophenoxy)benzamide:

ethylammonium 2-nitro-5-(2',4',6'-trichlorophenoxy)benzoate;

2-nitro-5-(2',4',6'-trichloroethanolammonium phenoxy)benzoate;

methyl 2-nitro-5-(2',3',4',5',6'-pentachlorophenoxy)benzoate;

n-pentyl 2-nitro-5-(2',4',6'-trichlorophenoxy)benzo-

2-nitro-5-(2',4'-dichlorophenoxy)benzoic acid; methyl 2-nitro-5-(2'-chlorophenoxy)benzoate;

methyl 2-nitro-5-(4'-chloro-3'-methylphenoxy)benzoate;

methyl 2-nitro-5-(3'-methylphenoxy)benzoate; ethyl 2-nitro-5-(2',6'-dichlorophenoxy)benzoate;

isopropyl 2-nitro-5-(2',4'-dichloro-6'-methylphenoxy)benzoate;

ethyl 2-nitro-5-(2'-chloro-4'-fluorophenoxy)benzo-

2-nitro-5-(2'-chloro-4'-fluorophenoxy)benzoic acid; methyl 2-nitro-5-(2',4'-dinitrophenoxy)benzoate;

2-nitro-5-(2',4'-dinitrophenoxy)benzoic acid;

2-nitro-5-(2'-chloro-4'-nitrophenoxy)benzoic acid; 2-nitro-5-[3'-(α , α , α -trifluoromethyl)-

isopropyl phenoxy]benzoate;

isopropyl 2-nitro-5-[3',5'-dicarbomethoxyphenoxy]benzoate:

methyl 2-nitro-5-(2'-methoxyphenoxy)benzoate; methyl 2-nitro-5-(4'-chloro-2'-nitrophenoxy)benzo-

2-nitro-5-(2',4'-dichloro-6'-fluorophenoxy)benzoic acid:

methyl 2-nitro-5-(2',4'-dichloro-6'-fluorophenoxy)benzoate;

2-nitro-5-(2',4'-dicarbomethoxyphenoxy)methyl benzoate: 2-nitro-5-[2'-cyano-4'-(α,α,α -trifluorome-

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methyl 2-nitro-5-(3'-carbomethoxy-4'-hydroxy-phenoxy)benzoate;

methyl 2-nitro-5-[4'-chloro-2'- $(\alpha,\alpha,\alpha$ -trifluorome-thyl)phenoxy]benzoate;

methyl 2-nitro-5-(3'-carbomethoxy-4'-nitrophenox-5y)benzoate;

methyl 2-nitro-5-(4'-chloro-2',6'-dibromophenoxy)-benzoate;

methyl 2-nitro-5-(2',4'-dicyanophenoxy)benzoate;

methyl 2-nitro-5-[2'-dimethylamino-4'- $(\alpha,\alpha,\alpha$ -tri-10 fluoromethyl)phenoxy]benzoate;

ethyl 2-nitro-5-[2'-amino-4'- $(\alpha,\alpha,\alpha$ -trifluoromethyl)phenoxy]benzoate;

methyl 2-nitro-5-[2'-methyl-4'-methylthiophenoxy]-benzoate;

N,N-dimethyl 2-nitro-5[2',6'-dimethyl-4'-methylthiophenoxy]benzamide;

methyl 2-nitro-5-[2'-methyl-4'-methylsulfonyl-phenoxy]benzoate;

ethyl 2-nitro-5-[2'-chloro-4'-methylsulfinylphenox-y]benzoate;

methyl 2-nitro-5-[4'-(N-trifluoromethylsulfonamide)phenoxy]benzoate;

methyl 2-nitro-5-(4'-cyanophenoxy)benzoate;

ethyl 2-nitro-5-(4'-carboethoxyphenoxy)benzoate; methyl 2-nitro-5-(4'-hydroxyphenoxy)benzoate

2-nitro-5-[2'-t-butýlphenoxy]benzoic acid;

2-nitro-5-[2'-carboxyphenoxy]benzoic acid; methyl 2-nitro-5-(4'-aminophenoxy)benzoate;

methyl 2-nitro-5-(4'-diethylaminophenoxy)benzoate:

methyl 2-nitro-5-(2'-methylaminophenoxy)benzoate;

methyl 2-nitro-5-(4'-mercaptophenoxy)benzoate; ethyl 2-nitro-5-(4'-methylthiophenoxy)benzoate;

methyl 2-nitro-5-(2'-sulfonamidophenoxy)benzoate; ethyl 2-nitro-5-(4'-methylsulfinylphenoxy)benzoate; methyl 2-nitro-5-(4'-methylsulfonylphenoxy)benzoate; ate; and

2-nitro-5-(2',4'-dichlorophenoxy)thiobenzoic acid. The following example illustrates the preparation of a typical compound of this invention and demonstrates a method for product recovery.

EXAMPLE 1

Methyl 2-nitro-5-(2',4',6'-trichlorophenoxy)benzoate

A stirred solution of methyl 5-chloro-2-nitro-benzoate (17.0 g., 0.79 mole) and the potassium salt of 2,4,6,-trichlorophenol (18.6 g., 0.79 mole) in dimethyl sulfoxide (100 ml.) was heated at 90° C for 17 hours. The cooled reaction mixture was diluted with water (500 ml.) and then extracted with ether (3×100 ml.). The combined ether fractions were washed with 10% sodium hydroxide solution (2×30 ml.) and then with a saturated aqueous sodium chloride solution. The ether solution was dried (Na₂SO₄) and the solvent evaporated to give a dark oil. Two crystallizations (petroleum ether) gave 1.91 g. of a pale yellow solid, m.p. 60 $101^{\circ}-103^{\circ}$ C.

EXAMPLE 1

IR(nujol): c=0 1723, c-0 1240, and 1260 cm⁻¹ NMR (CDCL₃): methyl 3.91 ppm (3H), quartet 6.96 65 ppm (1H, J = 2.5 and 8 c.p.s.), doublet 7.05 ppm (1H, J = 2.5 c.p.s.), broad singlet 7.05 ppm (2H), and doublet 8.01 ppm (1H, J = 8 c.p.s.).

EXAMPLES 2 through 24

Using procedures similar to that described in Example 1, twenty-three other compounds within the scope of this invention were prepared. These compounds are:

- 2. 2-nitro-5-(2',4',6'-trichlorophenoxy)benzoic acid, m.p. 184-189° C.
- 3. sodium 2-nitro-5-(2',4',6'-trichlorophenoxy)benzoate m.p. >300° C.
- 4. methyl 2-nitro-5-(2',4',5'-trichlorophenoxy)benzoate m.p. 100-103° C.
- 5. methyl 2-nitro-5-(2',4'-dichlorophenoxy)benzoate, m.p. 84°-86° C.
- 6. ethyl 2-nitro-5-(2',4',6'-trichlorophenoxy)benzoate, m.p. 60°-64° C.
- 7. methyl 2-nitro-5-(2',4'-dibromophenoxy)benzoate, m.p. 98°-100° C.
- 8. methyl 2-nitro-5-(4'-chloro-2'-methylphenoxy)benzoate, m.p. 70°-72° C.
 - 9. methyl 2-nitro-5-(2',4'-dimethylphenoxy)benzoate, oil.
- 10. 2-nitro-5-(2',4'-dichlorophenoxy)benzamide, m.p. 130°-133° C.
- 11. isopropyl 2-nitro-5-(2',4',6'-trichlorophenoxy)-benzoate, m.p. 71°-74° C.
 - 12. ethyl 2-nitro-5-(2',4'-dichlorophenoxy)benzoate, m.p. 83°-85° C.
- 30 13. isopropyl 2-nitro-5-(2',4'-dichlorophenoxy)benzoate, m.p. 59°-62° C.
 - 14. methyl 2-nitro-5-(2',4',6'-trichlorophenoxy)thiobenzoate, m.p. 96°-100° C.
 - 15. methyl 2-nitro-5-(2',4'-dichloro-6'-methylphenox-y)benzoate, m.p. 85°-89° C.
 - 16. methyl 2-nitro-5-(2'-chloro-4'-fluorophenoxy) benzoate, m.p. 67°-70° C.
 - 17. isopropyl 2-nitro-5-(2'-chloro-4'-fluorophenoxy) benzoate, m.p. 48°-51° C.
- 40 18. N-methyl 2-nitro-5-(2',4'-dichlorophenoxy) benzamide, m.p. 137° C.
 - 19. ethyl 2-nitro-5-(4',-nitrophenoxy) benzoate, m.p. 75°-82° C.
- 20. methyl 2-nitro-50(3'-methyl-4'-nitrophenoxy) benzoate, m.p. 75°-82° C.
 - 21. isopropyl 2-nitro-5-[2'-nitro-4'- $(\alpha,\alpha,\alpha,-\text{tri-fluoromethyl})$ phenoxy] benzoate, oil.
 - 22. ethyl 2-nitro-5-[2'-nitro-4'- $(\alpha,\alpha,\alpha,-\text{tri-fluoromethyl})$ phenoxy] benzoate, oil.
 - ²³ 23. methyl 2-nitro-5-[2'-chloro-4'-nitrophenoxy] benzoate, m.p. 97°–102° C.
 - 24. 2-nitro-5-(2'-chloro-4'-nitrophenoxy) benzoic acid, m.p. 185° C.

EXAMPLE 25

2-Nitro-5-[2'-nitro-4'-(α , α , α -trifluoromethyl)-phenoxy] benzoic acid

A stirred solution of 4-chloro-3-nitrobenzotrifluoride (22.55 g, 0.1 mole) and the potassium salt of 3-methyl-4-nitrophenol (19.12 g, 0.1 mole) in dimethyl acetamide (75 ml) was heated at 150° for 4 hours. The cooled reaction solution was diluted with water (300 ml) to precipitate a brown solid which was filtered and dried to give 28.9 g (85%) of 4-nitro-3-tolyl-2'-nitro- α , α , α -trifluoro-4'-tolyl ether, which has an m.p. of 82°-85° C.

To a stirred solution of the above diphenyl ether product (25.0 g, 0.073 mole) and sodium dichromate (35.8 g, 0.12 mole) in glacial acetic acid (200 ml) was added concentrated sulfuric acid (60 ml, 1.15 moles) over about 30 minutes. The temperature was maintained below 70° C during the addition and then raised to 110° C for 15 hours. The reaction solution was cooled to 60° C and extracted with hot chloroform. The extract was evaporated to dryness to give an oily solid, which was leached free of starting material with an ether-ligroin mixture. The resulting off-white solid acid weighed 13.6 g (51%), m.p. 185°-187°.

EXAMPLE 26

2-Nitro-5-[2'-nitro-4'-(α,α,α -trifluoromethyl)phenox- 15 y benzoic acid methyl ester

A stirred solution of the acid from Example 6'(3.5 g, 0.0094 mole) in a 25 wt. %/vol. solution of borontrifluoride in methanol (50 ml) was refluxed for 10 hours. The cooled solution was poured onto water (250 ml) and the resulting oil separated and dried to give 3.4 g (93.5%) of the desired product.

EXAMPLE 27

2-nitro-5-[2'-cyano-4'-(α,α,α ,-trifluoromethyl)phenoxy]benzoate

The sodium salt of 4-nitro-3-carbomethoxyphenol and 2-cyano-4- $(\alpha,\alpha,\alpha,-$ trifluoromethyl)chlorobenzene 30 in dimethylforamide were reacted at 150° C for 4 hours. Then, the reaction mixture was poured into water. The semi-solid precipitate which formed was extracted with diethyl ether and the ether extract was dried. The ether was removed, leaving a yellow oil 35 product.

COMPARATIVE EXAMPLES

A series of compounds were prepared which are position isomers of the compounds of Example 1 through 4. Each compound is designated by the number of the corresponding isomeric compound of Examples 1 through 4, followed by a or b. These compounds

1a. methyl 5-nitro-2-(2',4',6'-trichlorophenoxy)benzoate, m.p. 128°-133° C.

2a. 5-nitro-2-(2',4',6'-trichlorophenoxy)benzoic acid, m.p. 175°-177° C.

2b. 4-nitro-2-(2',4',5',-trichlorophenoxy)benzoic acid, 50 m.p. 190°-193° C.

3a. sodium 5-nitro-2-(2',4',6'-trichlorophenoxy)benzoate, m.p.>300° C.

4a. methyl 5-nitro-2-(2',4',5'-trichlorophenoxy)benzoate, m.p. 104°-106° C.

4b. methyl 4-nitro-2-(2',4',5'-trichlorophenoxy)benzoate, m.p. 127°-131° C.

As is apparent from the data in the Table set forth hereinafter, the compounds embodied herein in which 60 the nitro group is in the 2-position and the substituted phenoxy groups is in the 5-position exhibit markedly higher effectiveness as herbicides than do the comparable compounds in which the nitro group and the substituted phenoxy group are in different positions.

The compounds of this invention can be applied in various ways to achieve herbicidal action. They can be applied, per se, as solids or in vaporized form, but are

preferably applied as the toxic components in pesticidal compositions of the compound and a carrier. The compositions can be applied as dusts, as liquid sprays, or as gas-propelled sprays and can obtain, in addition to a carrier, additives such as emulsifying agents, binding agents, gases compressed to the liquid state, odorants, stabilizers, and the like. A wide variety of liquid and solid ca carriers can be used. Non-limiting examples of solid carriers include talc, bentonite, diatomaceous earth, pyrophyllite, fullers earth, gypsum, flours derived from cotton seeds and nut shells; and various natural and synthetic clays having a pH not exceeding about 9.5. Non-limiting examples of liquid carriers, include water; organic solvents, such as alcohols, ketones, amides and esters; mineral oils, such as kerosene, light oils, and medium oils and vegetable oils, such as cottonseed oil.

In practice, herbicidal application is measured in terms of pounds of herbicide applied per acre. The compounds of this invention are effective herbicides when applied in herbicidal amounts, i.e., at rates between about 0.2 pounds and about 10 pounds per acre.

HERBICIDAL EFFECTIVENESS

Method of Propagating Test Species Digitaria sanguinalis Crabgrass Setaria glauca Sorgum Halepense

Yellow Foxtail grass. Johnson grass Barnyard grass Amaranth pigweed Turnip Cotton

Amaranthus retroflexus Brassica sp. Gossypium hirsutum var. ... DPL Smooth leaf

Zea Mays var. Golden Bantam Corn Phaseolus vulgaris var. Bean Black Valentine

Echinochloa crus-galli

All crop and weed species are planted individually in 3 inch plastic pots containing potting soil. Four seeds of each of corn, cotton, and snapbeans are seeded to a depth equal to the diameter of the seed. All other species are surface seeded and sprinkled with screened soil in an amount sufficient to cover the seeds. Immediately after planting, all pots are watered by sub-irrigation in greenhouse trays. Pots for the pre-emergence phase are seeded one day before treatment.

Planting dates for the post-emergence phase are varied so that all the seedlings will reach the desired state of development simultaneously. The proper state of seedling development for treatment in the post-emergence phase is as follows

GRASSES: 15 PIGWEED & TURNIPS:

GOVERNMENT OF THE STATE OF

2 inches in height

1 or 2 true leaves visible above cotyledons. first true leaf 1 inch in length;

expanded cotyledons. 3 inches - 4 inches in height primary leaves expanded, growing point at primary leaf node.

BEANS:

COTTON:

CORN:

Method of Treatment

Spray applications are made in a hood containing movable belt and fixed spray nozzle. For passage 65 through the spray hood, one pot of each species (preemergence phase) is placed on the forward half of a wooden flat and one pot of established plants (postemergence phase) is placed on the rear half of the flat.

> signwait in a 2000 0000 000

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Treatments are moved to the greenhouse after spraying. Watering during the observation period is applied only by sub-irrigation.

Compounds are screened initially at a rate of application equivalent to 4 or 8 pounds per acre. Two weeks 5 after treatment the pre- and post- emergence per cent effectiveness is visually rated. Subsequent testing is carried out at 2, 1 and 0.5 pounds per acre.

Herbicidal testing of the compounds of Examples 1 through 27 and of the comparative compounds pro- 10 vided the results set forth in the Table. The plants are tabulated using the following abbreviations:

Crabgrass	CG VE	3	Pigweed	PW	
Yellow Foxtail grass	YF		Turnip	` TP	1 1 1 1
Johnson grass	JG.		Cotton	CT	
Barnyard grass	BG		Corn	CN	
Bean	BN	4.9			

modifications and variations may be resorted to without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the appended claims.

What is claimed is:

1. A compound having the formula:

wherein R is hydroxy or alkoxy of 1 to 5 carbon atoms, n is an integer of 2, and in which compound one X is trifluoromethyl and one other X is cyano.

2. A compound of claim 1, wherein said compound is

TABLE PRE/POST-EMERGENCE HERBICIDAL ACTIVITY* OF CERTAIN SUBSTITUTED PHENOXYBENZOIC ACIDS AND DERIVATIVES THEREOF

COMPOUND	COMPOUND						化自然分类系统		
OF EXAMPLE	CONCENTRATION, LBS./ACRE	CG	YF	JG	BG	PW	TP CT	CN	BN
1	4:	100/100	100/100	60/50	60/70	400/100	80/100 - 6 0/100	0/40	30/100
	2	100/100	80/100	30/70	20/80	100/100	0/100 . 7 90/100	30/20	70/100
	1	100/90	80/100	20/60	0/60	100/100	30/90 0/100	0/20	80/100
	0.5	40/50	60/80	30/60	0/40	100/70	.0/80 40/20	0/20	30/70
a(Comparativ	e) 4	20/20	0/20	0/20	0/20	20/0	0/30 100/0	50/0	20/80
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a(Comparativ	re) 4	20/30	0/20	20/30	0/20	—/20	30/90 50/20	0/0	50/70
b(Comparativ		0/30	40/0	50/30	20/20	20/20	0/50 40/20	30/30	80/0
Canaparata	4	50/80	/	30/60	40/60	-/-	95/100 50/100	0/40	50/100
a(Comparativ	(c) 4	0/20	0/20	0/20	0/20	50/50	0/60 100/0	30/0	50/40
.,		90/60	-/-	80/90	50/50	-/-	40/70 80/70	0/50	80/80
a(Comparativ	(c) 8	30/30	0/20	20/30	0/20	30/30	40/0 0/30	0/0	60/0
(Comparativ		20/20	0/20	0/20	0/20	0/20	0/60 30/50	0/30	0/60
o Companion	4	100/95	-/-	90/90	90/90	/	80/100 50/80	0/40	50/100
A carry	47.1	.100/80	_/_	80/50	50/70	100/100	40/90 30/100	0/100	100/100
18 4 34 34 34 54	8	80/60	-1-	50/40	60/50	100/100	20/100 30/90	. 0/50	100/100
	8	50/60	_/_	20/30	0/20	100/100	0/40 0/40	0/30	100/100
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y' l'adaSt,	A Prince of	80/70		40/40	40/30	100/100	20/70 100/40	0/20	100/100
Na sasaka sa k	4	60/70		30/60	20/50	90/100	0/50 30/70	0/30	80/60
2		90/90	_/_ _/_	90/90	60/90	1.00/100	0/100 0/100		0/100
To formation as a		100/90	/_	90/100	60/60	100/100	0/100 30/90	0/70	30/100
erect or small	9: 9:	100/100	100/—	40/60	80/70	<u></u>	30/100 80/70	0/70	100/100
	a in 🎁 Karabiga in wa	100/100	-/-	40/90	50/80	-/-	30/100 - 20/80	0/20	50/80
a september 1960	եներ ը ն հեղում օրդակա	70/90	_;_	30/90	20/80	90/100	0/30 30/70	0/20	100/100
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16	8	100/90	100/100 80/19	00 100/90	100/100	100/100	40/100	80/40	80/100
	4	100/100	100/100 100/19	00 80/80	100/100	70/100	40/90	20/80	80/100
	and the state of the state of	100/100	100/100 90/10		100/100	80/100	30/90	0/80	0/90
115	0.8	90/60	100/80 70/5	•	100/100	40/100	80/60	30/20	50/100
17	9	100/40	90/40 70/4		100/100	0/60	. 0/80	0/30	0/90
1 /		100/90	100/100 80/9		100/100	0/40	0/50	0/30	0/90
	4		100/100 80/3		100/100	20/30	0/50	0/30	0/90
	2	100/90			100/100	0/40	90/30	30/0	80/80
		60/50	100/80 90/6			90/100	30/80	0/80	0/100
18	8	90/80	-/- 60/8		-/-	/90	—/60	-/-	-/60
19	4 ·	40/30	-/- 90/-		-/		-/30 -/30	_/_	-/40
20	10	50/20	/ 90/-		-/-	20/20			-/40
21		100/—	100/— 30/-		50/—	30/	0/	0/	. 0/
22	1	90/—	100/ 100/-		-/-	30/—	50/—	60/	0/
23	10	80/—	100/- 100/-	- 30/	-/-	80/—	-/-	-/-	/
24	10	100/	/ 30/ - -	-/-	/	100/—	/	-/-	-/
25	8	80/60	90/100 50/4	30/60	100/100	100/100	30/50	0/30	30/90
26	R	100/80	100/90 40/2	90/60	100/100	90/90	0/50	0/20	70/90
-0	Ā	100/90	100/100 70/9		100/100	100/100	0/50	0/20	0/90
	3	90/70	100/100 60/6		100/100	90/90	0/50	0/30	0/90
27	4	100/100	_/_ 100/-		-/-	100/100	40/50	60/—	70/90
21	*			1 m m	-/-	100/90	30/40	· 20/	100/90
	r ≹ a ray is set de	90/90			_/_	100/100	20/40	20/	100/
	l	90/70	-/- 90/-	- 30/—		1.00/100	20,10		
		1941 117 1 1		A Variable gr		grafia series s	4	5 July 1878	to it
He	bicidal activity is measured in per ce	nt ettectiveness		The second second	14				
		Maria State of		a sewigal and the				11.	

Although the present invention has been described with preferred embodiments, it is to be understood that methyl 2-nitro-5-[2'-cyano-4'- $(\alpha,\alpha,\alpha,-$ trifluoromethyl)phenoxy]benzoate.

70/60

0/100

0/50

0/60

Page 1 of 2

UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent No	4,002,662	Dated January 11, 1977
		•
Inventor(s)	Robert J. Theissen	

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 27

"nitro-5-2',4',6'-trichlorophenoxy)" should be --nitro-5-(2',4',6'trichlorophenoxy) --

Column 3, line 24

"trifluoromethylsulfonamide)" should be --trifluoromethylsulfonamido)--

Column 8, Table

Example 19, under TP Column " /90"

should be -- 0/90 --

Column 8, Table

Example 21, under JG Column " 30/- "

should be -- 100/- --

Column 8, Table

Example 21, under BG Column " -/- "

should be -- 30/-

Column 8, Table

Example 21, under PW Column " 50/- "

should be -- -/-

Column 8, Table

Example 21, under TP Column " 30/- "

should be --50/-

UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent	No.	4,002,662	Dated	January	11,	1977
•	_		-			

Inventor(s) Robert J. Theissen

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, Table

Example 21, under CT Column " 0/- " should be -- 30/- --

Column 8, Table

Example 21, under BN Column " 0/- " should be inserted.

Bigned and Sealed this

Twenty-first Day of June 1977

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks